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ELECTROCHEMISTRY OF SULFUR ADLAYERS ON  
THE LOW-INDEX FACES OF SILVER

by

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## Electrochemistry of Sulfur Adlayers on the Low-Index Faces of Silver.

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**Abstract.** The formation and reactivity of sulfur adlayers on single-crystal Ag electrodes ((111), (110), and (100) orientations) in aqueous solutions (pH = 13) containing HS<sup>-</sup> is reported. Oxidative adsorption of HS<sup>-</sup> ( $\text{Ag} + \text{HS}^- \rightarrow \text{AgSH} + \text{e}^-$ ) occurs on all three low-index surfaces at potentials ranging between -0.5 and -0.7V of the thermodynamic value for bulk Ag<sub>2</sub>S formation. Voltammetric and electrochemical quartz crystal measurements demonstrate that the resulting AgSH adlayer undergoes a second one-electron oxidation ( $\text{AgSH} + \text{Ag} + \text{OH}^- \rightarrow \text{Ag}_2\text{S} + \text{H}_2\text{O} + \text{e}^-$ ) at the (111) and (110) surfaces prior to bulk Ag<sub>2</sub>S formation, yielding an underpotential deposited Ag<sub>2</sub>S adlayer (surface coverages (S/Ag):  $\theta_{\text{Ag}(111)} = 0.46 \pm 0.02$  and  $\theta_{\text{Ag}(110)} = 0.54 \pm 0.03$ ). In contrast, the AgSH adlayer on Ag(100) is chemically inert prior to bulk Ag<sub>2</sub>S formation. Structural models indicate that the formation of a nearly stoichiometric Ag<sub>2</sub>S adlayer (i.e.,  $\theta \sim 0.5$ ) is feasible on the (111) and (110) surfaces without significant reconstruction of the outermost atomic layers of the substrate, but not on the (100) surface. The results suggest that the formation of a Ag<sub>2</sub>S monolayer is allowed only when the number density of S and Ag atoms at the interface is nearly coincident with the reaction stoichiometry.

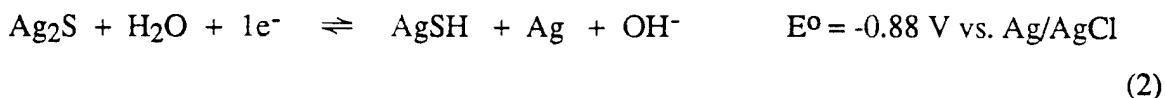
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**Introduction.** Metal oxidation reactions yielding stable films comprising a metal cation and charge-balancing anion, especially metal oxides, are of general interest in fields of catalysis, corrosion, and microelectronics device fabrication. Specifically, technologies based on metal oxidation chemistry frequently require precise control or knowledge of the morphology and electronic structure of films of molecular dimensions. During the past decade, emphasis has been placed on revealing atomic-level structural details of such thin films using high-resolution surface analytical techniques, e.g., scanning tunneling microscopy<sup>1</sup> and low energy electron diffraction.<sup>2</sup> In addition to surface structural tools, electrochemical methods are particularly well-suited to investigations of solution-phase metal oxidation since the surface oxidation state can be continuously and precisely controlled by varying the electrostatic potential of the metal/solution interface.<sup>3-11</sup> For example, in a recent report from this laboratory, we described the electrochemical deposition and reactivity of sulfur adlayers at Ag(111) electrodes immersed in an aqueous solution (pH 13) containing HS<sup>-</sup>.<sup>12</sup> The adsorption of HS<sup>-</sup> onto Ag surfaces represents the initial step in the growth of a thin Ag<sub>2</sub>S layer on Ag,<sup>13-16</sup> a process that is representative of the oxidation of many metal surface. Our previous electrochemical studies have revealed that deposition of the first monolayer of Ag<sub>2</sub>S proceeds through a potential-dependent mechanism involving at least two chemically distinct species of adsorbed S at the Ag(111)/H<sub>2</sub>O interface.<sup>1</sup> We now report details of the absorption and reactivity of HS<sup>-</sup> on all three low-index Ag surfaces.

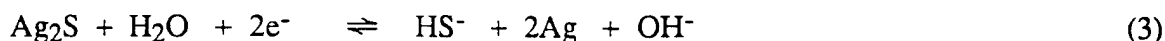
The formation of a sulfur adlayer at Ag(111) begins at potentials ~0.5 V negative of the thermodynamic redox potential for bulk oxidation of Ag in a HS<sup>-</sup> solution ( $E^{\circ}(\text{Ag}/\text{Ag}_2\text{S}) = -0.88 \text{ V vs. Ag}/\text{AgCl}$ ).<sup>17</sup> The results of previous coulometric, voltammetric, and in-situ electrochemical quartz crystal microbalance (EQCM) mass measurements indicate that the initial adlayer results from the reversible 1-e<sup>-</sup> oxidative adsorption of HS<sup>-</sup>, i.e., adsorption of HS<sup>-</sup> is a redox



process resulting in a AgSH surface complex.<sup>12</sup> At more positive potentials, but again prior to bulk Ag oxidation, the adsorbed layer is further oxidized yielding a monolayer of Ag<sub>2</sub>S, eq. (2). The Ag/S stoichiometry indicated in eq. (2) is based on the potential-dependent



number density of S adatoms per Ag atom on the (111) surface (i.e., the surface coverage or packing density,  $\theta$ ) determined by in-situ EQCM and coulometric measurements.<sup>12</sup> Specifically, a negligible change in the mass of the adsorbed layer is observed during the second surface oxidation reaction, consistent with eq. (2) which indicates that the only anticipated mass change is that corresponding to expulsion of protons from the interface. Combining eqs. (1) and (2) yields the overall reaction for deposition of a monolayer of Ag<sub>2</sub>S on the Ag(111) surface.



Because eq. (3) describes both bulk and surface Ag oxidation, the deposition of a monolayer of Ag<sub>2</sub>S at potentials prior to bulk Ag oxidation is similar to the more well-studied underpotential deposition (upd) of metal atoms on a foreign metal electrode<sup>18</sup> (e.g., Pb deposition on Ag<sup>19</sup>). In the latter case, the reductive deposition of a monolayer of metal atoms ( $\text{M}^{z+} + z\text{e}^- \rightleftharpoons \text{M}$ ) is observed at potentials positive of the thermodynamic potential for bulk metal deposition,  $E^0(\text{M}^{z+}/\text{M})$ . The initial potential-dependent adsorption of anions (in metal oxidation) or cations (in upd films) are physically similar processes; however, the continued growth of metal oxidation layers, such as Ag<sub>2</sub>S on Ag, is inherently more complex than metal deposition reactions, due to the fact that oxidative film growth requires chemical reaction between two species (bulk metal atom and solution anion) that are separated by a product film.

Adsorption of HS<sup>-</sup> (eq. (1)) is also analogous to the oxidative adsorption of halogens on Ag (eq. (4), X = I, Br, and Cl) at potentials negative of the thermodynamic potential for bulk AgX formation.<sup>20,21</sup> However, the Ag/sulfur appears unique among

metal/anion adlayer systems in that the final adlayer structure results from two discrete 1-e<sup>-</sup> oxidative steps, eqs. (1) and (2).



In current work, we have extended our studies of sulfur adlayers to all three low-index surfaces of Ag single-crystal electrodes. We observe that oxidative adsorption of HS<sup>-</sup> (eq. (1)) occurs at all three surfaces at potentials negative of E<sup>0</sup>(Ag/Ag<sub>2</sub>S). As anticipated, the potential at which HS<sup>-</sup> adsorption occurs, and the resulting surface coverages are strongly dependent on the surface orientation of the Ag electrode. However, in addition to these expected dependencies, the chemical reactivity of adsorbed HS (eq. (2)) is surprisingly sensitive to crystallographic orientation of the Ag electrode. In particular, oxidation of AgSH to an upd Ag<sub>2</sub>S monolayer occurs at the (111) and (110) surfaces, but not on the (100) surface. The dependence of the AgSH adlayer reactivity on crystallographic orientation is interpreted in terms of the relationship between allowed packing densities and surface reaction stoichiometry.

### Experimental.

*Electrochemical Cell and Apparatus.* A standard one-compartment cell containing Pt and Ag/AgCl (3M NaCl) auxiliary and reference electrodes, respectively, and equipped with ports for inlet and outlet N<sub>2</sub> flow, was used for all experiments. All solutions contained 0.75 mM Na<sub>2</sub>S and 0.2M NaOH. The primary S species present in this solution is hydrosulfide, HS<sup>-</sup> (>99.99 %), as determined from the literature pK<sub>a</sub> values for H<sub>2</sub>S (7.02) and HS<sup>-</sup> (17.1).<sup>22</sup> Solutions were purged for ~20 minutes with N<sub>2</sub> to remove O<sub>2</sub> from the solution, and a positive pressure of N<sub>2</sub> was maintained in the electrochemical cell. Measurements were made at 25 ± 2°C. Voltammetric data were obtained using a Princeton Applied Research Corp. (PARC) Model 173 Potentiostat and a Model 175 Universal Programmer. A Kipp and Zonen Model BD-90 x-y recorder was used to record voltammetric curves.

*Electrochemical Quartz Crystal Microbalance.* The EQCM is identical to that described in our earlier studies<sup>12</sup> and is based on a design by Ward.<sup>23</sup> Preparation of (111)-oriented

Ag-coated EQCM crystals, as well as detailed procedures for frequency calibration and evaluation of the mass detection limit in  $\text{HS}^-$  solutions, have been previously reported.<sup>12</sup>

*Chemicals.* All solutions were prepared using water obtained from a Barnstead "E-pure" water purification system. NaOH (Mallinckrodt, 98.8%),  $\text{Na}_2\text{S}$  (Mallinckrodt, 98.8%), NaCN (Mallinckrodt, 98.8%) were used as received.

*Preparation of Ag Single Crystal Electrodes.* Ag single crystals were obtained from Monocrystals Company. The exposed surface areas of the (111)-, (110)-, and (100)-oriented electrodes were  $0.30\text{ cm}^2$ ,  $0.64\text{ cm}^2$ , and  $0.64\text{ cm}^2$ , respectively. Each crystal was embedded into a Kel-F rod, and a Ag wire was attached to the embedded side with conductive Ag epoxy (5504N, Dupont). The electrodes were polished using progressively finer grades of alumina powder (from  $1.5\text{ }\mu\text{m}$  to  $0.01\text{ }\mu\text{m}$  diameter) until a mirror surface was obtained on the Ag surface. Immediately prior to voltammetric measurements, the single-crystal electrodes were chemically polished using a procedure originally described by Bewick et al.<sup>24</sup> Because the voltammetric response is critically dependent upon surface preparation, we briefly describe this procedure. Initially, the electrode is immersed in a freshly prepared solution containing equal volumes of aqueous  $0.43\text{ M NaCN}$  and  $20\%\text{ H}_2\text{O}_2/\text{H}_2\text{O}$  (v/v). After  $\sim 3\text{ s}$ , gas evolution is observed at the surface of the Ag electrode. The electrode was removed from this solution to air with a thin film of the etching solution clinging to the electrode surface. After a few seconds in air, gas evolution from the electrode surface is visible in the thin solution film. The electrode is then placed in a  $0.77\text{ M NaCN}$  solution until visible gas evolution ceases. This procedure is repeated  $\sim 10$  times until a mirror finish is obtained on the exposed Ag surface. The electrode is then washed with purified  $\text{H}_2\text{O}$  and transferred to the electrochemical cell. Reproducible electrochemical results at all three low-index faces were obtained following this procedure.

## Results and Discussion.

*Ag(111).* The voltammetric response of the Ag(111) single-crystal electrode in an aqueous solution containing  $0.75\text{ mM Na}_2\text{S}$  and  $0.2\text{ M NaOH}$  is shown in Fig. 1. An anodic wave (labeled  $D_a$ ) is observed on the positive-going scan at potentials slightly positive of  $E^0(\text{Ag}/\text{Ag}_2\text{S})$ . This anodic wave corresponds to the oxidation of bulk Ag, leading to the deposition of a relatively thick  $\text{Ag}_2\text{S}$  film, eq. (3), as had been previously

determined using polycrystalline Ag electrodes.<sup>13-15</sup> Several smaller peaks can be discerned within wave D<sub>a</sub>, suggesting that bulk deposition of Ag<sub>2</sub>S at the Ag(111) surface occurs in a multistep process that is resolvable by voltammetric measurements. However, we have not pursued this finding. Upon reversing the direction of the potential scan, the Ag<sub>2</sub>S layer is cathodically reduced, as evidenced by a large stripping peak (D<sub>c</sub>) at potentials slightly negative of E<sup>0</sup>(Ag/Ag<sub>2</sub>S). From coulometric integration of the area under the stripping wave, the thickness of the Ag<sub>2</sub>S layer generated during this specific voltammetric experiment is estimated to be equivalent to ~8 monolayers of Ag<sub>2</sub>S.<sup>25</sup> The onset of bulk Ag<sub>2</sub>S deposition is shifted positive from E<sup>0</sup>(Ag/Ag<sub>2</sub>S) by ca. 0.05 V, indicating a significant kinetic barrier to growth of Ag<sub>2</sub>S on Ag(111). The irreversible nature of eq. (3) is also apparent in the relatively large potential splitting of the Ag<sub>2</sub>S deposition and reduction waves.

At potentials negative of the bulk Ag<sub>2</sub>S deposition and reduction wave (D<sub>a</sub>/D<sub>c</sub>), several smaller waves are observed that are associated with adsorption and reaction of HS<sup>-</sup> at the Ag(111) surface. Higher-resolution voltammetry in this potential region (Fig. 2b) shows a set of three well-resolved surface waves (A<sub>a</sub>/A<sub>c</sub>, B<sub>a</sub>/B<sub>c</sub>, and C<sub>a</sub>/C<sub>c</sub>) with half-wave potentials, E<sub>1/2</sub>, equal to -1.21V, -1.03, and -0.87 V vs. Ag/AgCl, respectively (where E<sub>1/2</sub> = (E<sub>pc</sub> + E<sub>pa</sub>)/2, and E<sub>pc</sub>/E<sub>pa</sub> are the cathodic/anodic peak potentials). All three surface voltammetric waves are absent in the voltammetric response obtained in solutions containing only 0.2 M NaOH.

The voltammetric response of the Ag(111) single-crystal electrode shown in Fig. 2b is essentially identical to the responses previously reported for polycrystalline (111)-oriented Ag film electrodes deposited on mica, or quartz surfaces used for the EQCM. All three surface waves (A<sub>a</sub>/A<sub>c</sub>, B<sub>a</sub>/B<sub>c</sub>, and C<sub>a</sub>/C<sub>c</sub>) are observed at the polycrystalline Ag film electrodes, with E<sub>1/2</sub> values within 10 mV of the values obtained at the single crystal electrode. Based on previous experimental studies employing mica/Ag(111) and EQCM/Ag(111) electrodes (detailed in ref. 12), we have assigned waves A<sub>a</sub>/A<sub>c</sub> and B<sub>a</sub>/B<sub>c</sub> to oxidative adsorption of HS<sup>-</sup> (eq. (1)), resulting in the formation of the AgSH adlayer. Wave C<sub>a</sub>/C<sub>c</sub> corresponds to subsequent oxidation of the AgSH adlayer (eq. (2)), producing a complete Ag<sub>2</sub>S upd layer prior to bulk oxidation of Ag. Briefly, key evidence supporting this interpretation is obtained from in-situ EQCM measurements of the



interfacial mass changes associated with each voltammetric wave. The frequency response of the EQCM/Ag(111), obtained under identical experimental conditions as those used to measure the voltammetric response at the Ag(111) single-crystal electrode, is reproduced in Fig. 2a. A reversible  $2.15 \pm 0.30$  Hz ( $2\sigma$ ) frequency shift is observed when the potential is scanned through voltammetric waves  $A_a/A_c$  and  $B_a/B_c$ , consistent with these waves corresponding to the reversible oxidative adsorption of  $HS^-$ . In comparison, a negligibly small frequency change is observed in the potential range of wave  $C_a/C_c$ , clearly demonstrating that this wave is not associated with a significant increase in the interfacial mass.

The Sauerbrey equation (eq. (5)) allows the frequency response of the EQCM,  $\Delta f$ , to be quantitatively related to the interfacial mass change,  $\Delta m$ .

$$\Delta f = -2f_0 \Delta m / A(\mu_q \rho_q)^{1/2} \quad (5)$$

In eq. (5),  $f_0$  is the parent resonance frequency of the crystal ( $\sim 5 \times 10^6$  Hz),  $A$  is the area of shear motion ( $0.178 \text{ cm}^2$ ), and  $\mu_q$  and  $\rho_q$  are the shear modules ( $2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-1}$ ) and density ( $2.648 \text{ g cm}^{-3}$ ) of quartz, respectively. Using these values, the observed  $2.15 \pm 0.30$  Hz frequency shift for waves  $A_a/A_c$  and  $B_a/B_c$  corresponds to an adsorbed mass of  $3.8 \pm 0.5 \times 10^{-8} \text{ g/cm}^2$ , or assuming that  $HS^-$  is the adsorbing species, to a surface coverage,  $\Gamma_{HS}$ , of  $1.19 \pm 0.16 \times 10^{-9} \text{ mol/cm}^2$ . In comparison, coulometric integration of the anodic (or cathodic) peaks of waves  $A_a/A_c$  and  $B_a/B_c$  yields  $\Gamma_{HS} = 1.16 \times 10^{-9} \text{ mol/cm}^2$ , assuming a  $1\text{-e}^-$  oxidation, eq. (1). The excellent agreement between the values of  $\Gamma_{HS}$  determined by coulometry and EQCM mass measurements strongly supports our contention that waves  $A_a/A_c$  and  $B_a/B_c$  result from oxidative adsorption of  $HS^-$ , eq. (1). The fact that two waves are associated with interfacial mass changes ( $A_a/A_c$  and  $B_a/B_c$ ) suggests that at least two energetically-distinct sites of  $HS^-$  adsorption exist at the (111) surface.

Further experimental support of our assignment of waves  $A_a/A_c$  and  $B_a/B_c$  to eq. (1) and wave  $C_a/C_c$  to eq. (2) is based on the dependence of the magnitude and shapes of these waves on the voltammetric scan rate. The peak currents associated with waves  $A_a/A_c$  and  $B_a/B_c$  at the single-crystal (111)-oriented electrode increase linearly with scan rate ( $v$ )

for  $30 < v < 100$  mV, Fig. 3, consistent with rapid establishment of an equilibrium surface coverage of HS on the voltammetric time scales. The symmetry of the anodic and cathodic peaks of each of these waves, which is independent of scan rate, also suggests that an equilibrium surface coverage is maintained throughout this potential region. In comparison, the peak splitting of wave  $C_a/C_c$  is significant, e.g., 50 mV at  $v = 100$  mV/s, Fig. 2b, and increases markedly with increasing scan rate. Furthermore, we find that the magnitude of wave  $C_a/C_c$  is not proportional to  $v$ , but rather to  $v^{2/3}$ , Fig. 3. Both of these latter observations are consistent with the AgSH-to-Ag<sub>2</sub>S adlayer transition (eq. 2) occurring by a two-dimensional nucleation and growth process.<sup>26</sup> The results suggest that the oxidation of the AgSH layer to a Ag<sub>2</sub>S layer results in a more ordered layer, analogous to potential-dependent order/disorder transitions determined by LEED for halogen adsorption on Ag(111).<sup>27</sup>

Coulometric integration of the anodic peaks of the three voltammetric waves ( $A_a$ ,  $B_a$ , and  $C_a$ ) leading to the formation of the upd Ag<sub>2</sub>S layer yields a charge of  $204 \pm 10$   $\mu\text{C}/\text{cm}^2$ . Assuming  $n = 2$  for the overall deposition of the upd Ag<sub>2</sub>S adlayer (eq. (3)) allows the surface coverage,  $\theta_{(111)}$ , (i.e., the ratio of S atoms per Ag(111) surface atom) to be computed as  $0.46 \pm 0.02$ . The corresponding value determined from the EQCM/Ag(111) measurement is  $0.52 \pm 0.07$ , within error of the electrochemical results. Values of  $\theta_{(ijk)}$  are used in a later section in proposing structures for the Ag<sub>2</sub>S adlayer for each surface orientation.

**Ag(110).** The voltammetric response of the Ag(110) single-crystal electrode in HS<sup>-</sup> solutions is qualitatively similar to that described above for Ag(111) electrodes. Oxidation of bulk Ag occurs at potentials slightly positive of  $E^0(\text{Ag}_2\text{S}/\text{Ag})$ , resulting in a multilayer Ag<sub>2</sub>S film that can be readily reduced off at potentials slightly negative of  $E^0(\text{Ag}_2\text{S}/\text{Ag})$ . Four voltammetric waves ( $A_a/A_c$ ,  $B_a/B_c$ ,  $B_a'/B_c'$ , and  $C_a/C_c$ ) corresponding to adsorbed HS are observed with  $E_{1/2}$  values of -1.36, -1.23, -1.18, and -1.09 V vs. Ag/AgCl, Fig. 2c. The close similarity of the voltammetric responses for Ag(111) and Ag(110) electrodes clearly suggests that waves  $A_a/A_c$  and  $C_a/C_c$  for both electrodes are associated with the same chemical processes. Wave  $B_a/B_c$  at the Ag(110) surface, however, appears split into two waves ( $B_a/B_c$  and  $B_a'/B_c'$ ) at the Ag(110) surface. Adsorption of HS<sup>-</sup> at the Ag(110)

surface begins at potentials  $\sim 150$  mV negative than on the Ag(111) surface. This shift most likely reflects the difference in the work function ( $\Phi$ ) of these two surfaces ( $\Phi_{(111)} = 4.74$  eV and  $\Phi_{(110)} = 4.52$  eV<sup>28</sup>).

The scan rate dependencies of the magnitude and shape of the voltammetric waves associated with the Ag(110) electrode are identical to that observed for the Ag(111) electrode. Waves  $A_a/A_c$ ,  $B_a/B_c$ , and  $B_a'/B_c'$  increase linearly in relation to  $v$ , with minimal peak splitting up to  $v = 250$  mV/s, Fig. 3. Wave  $C_a/C_c$  shows a pronounced peak splitting at higher scan rates, and the peak currents for this wave are proportional to  $v^{2/3}$ , rather than  $v$ .

Based on the similarities in the voltammetric behaviors of the (111) and (110)-oriented electrodes, we assign waves  $A_a/A_c$ ,  $B_a/B_c$ , and  $B_a'/B_c'$  to oxidative adsorption of  $HS^-$ , eq. (1). Similarly, wave  $C_a/C_c$  is assigned to the oxidation of the AgSH adlayer, yielding a  $Ag_2S$  adlayer, eq. (2). Coulometric integration of all four voltammetric waves yields a surface charge density of  $145 \pm 8 \mu C/cm^2$ . Assuming that  $Ag_2S$  is the final adlayer structure, the surface coverage on the (110) surface,  $\theta_{(110)}$ , is computed to be  $0.54 \pm 0.03$ .

**Ag(100).** The voltammetric response of the Ag(100) electrode in the 0.75 mM  $Na_2S/0.2M$  NaOH solution is presented in Fig. 2d. Similar to observations at the (111)- and (110)-oriented electrodes, the deposition and stripping of a multilayer film of  $Ag_2S$  occurs at potentials centered on  $E^0(Ag_2S/Ag)$ . The shape of this bulk wave is qualitatively similar to wave  $D_a/D_c$  for the Ag(111) electrode, Fig. 1. The voltammetric behavior associated with adsorbed  $HS^-$  at the (100) surface, however, is considerably different from the responses at either the (111) or (110) surface. Only two waves,  $A_a/A_c$  and  $B_a/B_c$ , with  $E_{1/2}$  values of  $-1.39$  and  $-1.21$  V vs. Ag/AgCl, respectively, are observed prior to bulk  $Ag_2S$  deposition. Both of these voltammetric waves display scan rate dependencies characteristic of oxidative adsorption of  $HS^-$ , Fig. 3, analogous to waves  $A_a/A_c$  and  $B_a/B_c$  at the (111)- and (110)-oriented electrodes. Specifically, the peak currents for these two symmetrically-shaped wave increase in proportion to  $v$ , and there is minimal peak splitting at higher scan rates. In addition, the initial adsorption of  $HS^-$  on the (100) surface is shifted negative by  $\sim 180$  mV with respect to adsorption on the (111) surface, consistent

with literature values of the work functions of these two surfaces ( $\Phi_{(111)} = 4.74$  eV and  $\Phi_{(100)} = 4.64$  eV).<sup>27</sup>

Based on the above experimental evidence, we assign waves  $A_a/A_c$  and  $B_a/B_c$  to the oxidative adsorption of  $HS^-$ . Integration of the current associated with the anodic peaks of waves  $A_a/A_c$  and  $B_a/B_c$  yields  $54 \pm 4 \mu C/cm^2$ , equivalent to an HS coverage,  $\Gamma_{HS} = 5.6 \pm 0.4 \times 10^{-10}$  mol/cm<sup>2</sup>, or a sulfur surface coverage,  $\theta_{(100)}$ , of  $0.28 \pm 0.02$ .

The most interesting feature of the voltammetric response of the Ag(100) electrode is the clear absence of a wave corresponding to oxidation of the AgSH adlayer. In contrast to the Ag(111) and Ag(110) electrodes, which display a well defined voltammetric wave ( $C_a/C_c$ ) corresponding to the formation of an upd  $Ag_2S$  adlayer, the Ag(100) electrode response is featureless at potentials intermediate between oxidative adsorption of  $HS^-$  and the deposition of bulk  $Ag_2S$ , Fig. 2. These results unequivocally demonstrate that the  $Ag_2S$  adlayer is energetically unfavorable relative to bulk  $Ag_2S$  on the (100) surface, but not on the (111) or (110) surfaces. This difference in surface energetics is clearly associated with differences in the atomic arrangement of sulfur adatoms on the three crystallographic surfaces, a point that is discussed below in more detail.

**Proposed Sulfur Adlayer Structures.** Fig. 4 shows proposed models of the sulfur adlayer structures on the three low-index faces of Ag. The coverages of sulfur adatoms indicated in these drawings are consistent with the measured values determined by coulometry ( $\theta_{(111)} = 0.46 \pm 0.02$ ,  $\theta_{(110)} = 0.54 \pm 0.03$ ,  $\theta_{(100)} = 0.28 \pm 0.02$ ). Admittedly, the electrochemical measurements presented in the previous sections do not directly provide structural details of the sulfur adatom position relative to the lattice of Ag atoms. Atomic level details of these adlayer structures, in contact with the electrolyte solutions, require in-situ surface-sensitive structural analysis using, for instance, STM or surface extended X-ray adsorption fine structure measurements (SEXAFS). However, consideration of the adlayer structures is necessary as a guide in order to rationalize (i) the differences in the  $\theta_{(ijk)}$  values, and (ii) the observation that a  $Ag_2S$  adlayer is energetically favorable on the (111) and (110) surfaces at potentials negative of  $E^0(Ag_2S/Ag)$ , but not on the (100) surface.

The in-situ EQCM mass measurements on Ag(111) surfaces demonstrate that a negligible increase in interfacial mass occurs upon oxidation of AgSH to Ag<sub>2</sub>S. Thus,  $\theta_{(ijk)}$  values are independent of the whether a AgSH or Ag<sub>2</sub>S adlayer is being considered. However, the models in Fig. 4 correspond to full S monolayer coverages which are obtained at potentials positive of the B<sub>a</sub>/B<sub>c</sub> wave for the (111)- and (100)-oriented electrodes, and at potentials positive of wave B<sub>a</sub>'/B<sub>c</sub>' for the (110)-oriented electrode.

A ( $\sqrt{7} \times \sqrt{7}$ )R10.9 adlayer structure is proposed for the Ag(111) surface, corresponding to a theoretical surface coverage,  $\theta_{(111)}$ , of 0.44. The corresponding value obtained from integration of the voltammetric wave is  $0.46 \pm 0.02$ . The ( $\sqrt{7} \times \sqrt{7}$ )R10.9 structure, in which S adatoms occupy three-fold hollow and top sites, has been reported for sulfur adlayers obtained in ultra-high vacuum by dosing Ag(111) with H<sub>2</sub>S.<sup>29</sup> Although this latter result supports our assignment, the adlayer structures in the liquid and vacuum environments need not necessarily be coincident, due to the interactions of solvent and electrolyte ions with the surface. Preliminary attempts at in-situ STM imaging of mica/Ag(111) electrodes under potential control in the Na<sub>2</sub>S/NaOH solution have not been successful in revealing the adlayer structure. However, ex-situ examination of the Ag(111) surface after deposition of a Ag<sub>2</sub>S adlayer shows a hexagonal arrangement of sulfur adatoms separated by  $\sim 4.6 \text{ \AA}$ ,<sup>30</sup> consistent with the theoretical value of  $4.56 \text{ \AA}$  for the model proposed in Fig. 4.

A c(2x3) adlayer structure at the Ag(110) surface is shown in Fig. 4. This structure corresponds to  $\theta_{(110)} = 0.5$ , in agreement with experimental value of  $0.54 \pm 0.03$ . In drawing the adlayer structure, we have place the S adatoms in two-fold sites along the outermost rows of Ag atoms, which, in the absence of surface reconstruction, would appear to be the most energetically-favored position of adsorption.

The c(2x4) adlayer structure proposed in Fig. 4 for the (100) surface corresponds to a theoretical surface coverage of 0.25, in reasonable agreement with the experimental value of  $0.29 \pm 0.02$ . The surface coverage is a factor of  $\sim 2$  lower on the (100) surface than on the other two low-index faces of Ag, a finding that must result from repulsive lateral interactions between sulfur atoms on the (100) surface. The ionic ( $1.84 \text{ \AA}$ )<sup>31</sup> and van der Waals ( $\sim 1.8 \text{ \AA}$ )<sup>32</sup> radii for S are both significantly larger than the atomic radius of Ag ( $1.44 \text{ \AA}$ ).<sup>33</sup> Thus, it is not surprising that the  $\theta_{(ijk)}$  values are considerably less than

unity on all three low index surfaces. The nearest-neighbor distances corresponding to the periodic adlayer structures shown in Fig. 4 are 4.56 Å (111), 4.99 Å (110), and 6.46 Å (100), each significantly greater than the ionic or van der Waals radii of S. Other common adlayer structures on the Ag(100) surface which correspond to higher surface coverages, would yield nearest-neighbor distances that are considerably shorter. For instance, a  $c(2 \times 2)$  adlayer model would result in a nearest-neighbor distance of 4.08 Å, corresponding to the S adatoms being within  $\sim 0.2$  Å of each other. Such a densely packed structure would be energetically unfavorable due to large repulsive adsorbate-adsorbate interactions.

The observation that the AgSH adlayer can not be further oxidized to an up  $\text{Ag}_2\text{S}$  adlayer at the (100) surface is interpreted as being related to the low surface coverage on this surface. In the previous report of  $\text{Ag}_2\text{S}$  adlayer formation on mica/Ag(111),<sup>12</sup> it was shown that voltammetric wave  $C_a/C_c$ , corresponding to the AgSH-to- $\text{Ag}_2\text{S}$  transition, is completely absent when the surface coverage of HS was lowered below a critical value ( $\theta \sim 0.32$ ). In these previous experiments, submonolayer coverages of HS were obtained by lowering the concentration of  $\text{HS}^-$  in the contacting solution. The results presented above indicate that the HS surface coverages are sufficiently large on the (111) and (110) surfaces to allow the oxidative AgSH-to- $\text{Ag}_2\text{S}$  transition. The most probable reason for the existence of a critical surface coverage is that the  $\text{Ag}_2\text{S}$  adlayer has a long-range crystalline order, stabilized by electrostatic interactions within the two-dimensional  $\text{Ag}_2\text{S}$  array (similar to that in bulk solids, e.g.,  $\text{Ag}_2\text{S}$ ). This lattice energy may not be available when the sulfur surface coverage is sufficiently low, a situation corresponding to sub-monolayer coverages on the (111) surface<sup>12</sup>, or full monolayer coverage on the (100) surface.

## Conclusion.

Reversible oxidative adsorption of  $\text{HS}^-$  from basic solutions occurs on all three low-index Ag surfaces. Combined coulometric and EQCM measurements of the interfacial charge and mass, respectively, associated with adsorption of  $\text{HS}^-$  at Ag(111) electrodes indicates that adsorption is a 1- $e^-$  redox process, consistent with the formation of a AgSH adlayer. The multiwave voltammetric pattern for  $\text{HS}^-$  adsorption indicates that multiple and energetically-distinct adsorption sites exist on each crystallographic surface. Future investigations using in-situ structural methods will be required to determine the potential

dependent adlayer structures. In addition, we have shown that the oxidation of the AgSH adlayer to an upd Ag<sub>2</sub>S adlayer occurs at the (111) and (110) surfaces, but not at the (100) surface. The voltammetric response associated with this redox transition displays features characteristic of nucleation and growth of an ordered two-dimensional phase. Our results suggest that the formation of the Ag<sub>2</sub>S adlayer is energetically favored at high surface coverages, due to the lattice energy stabilization of the ordered two-dimensional Ag<sub>2</sub>S phase.

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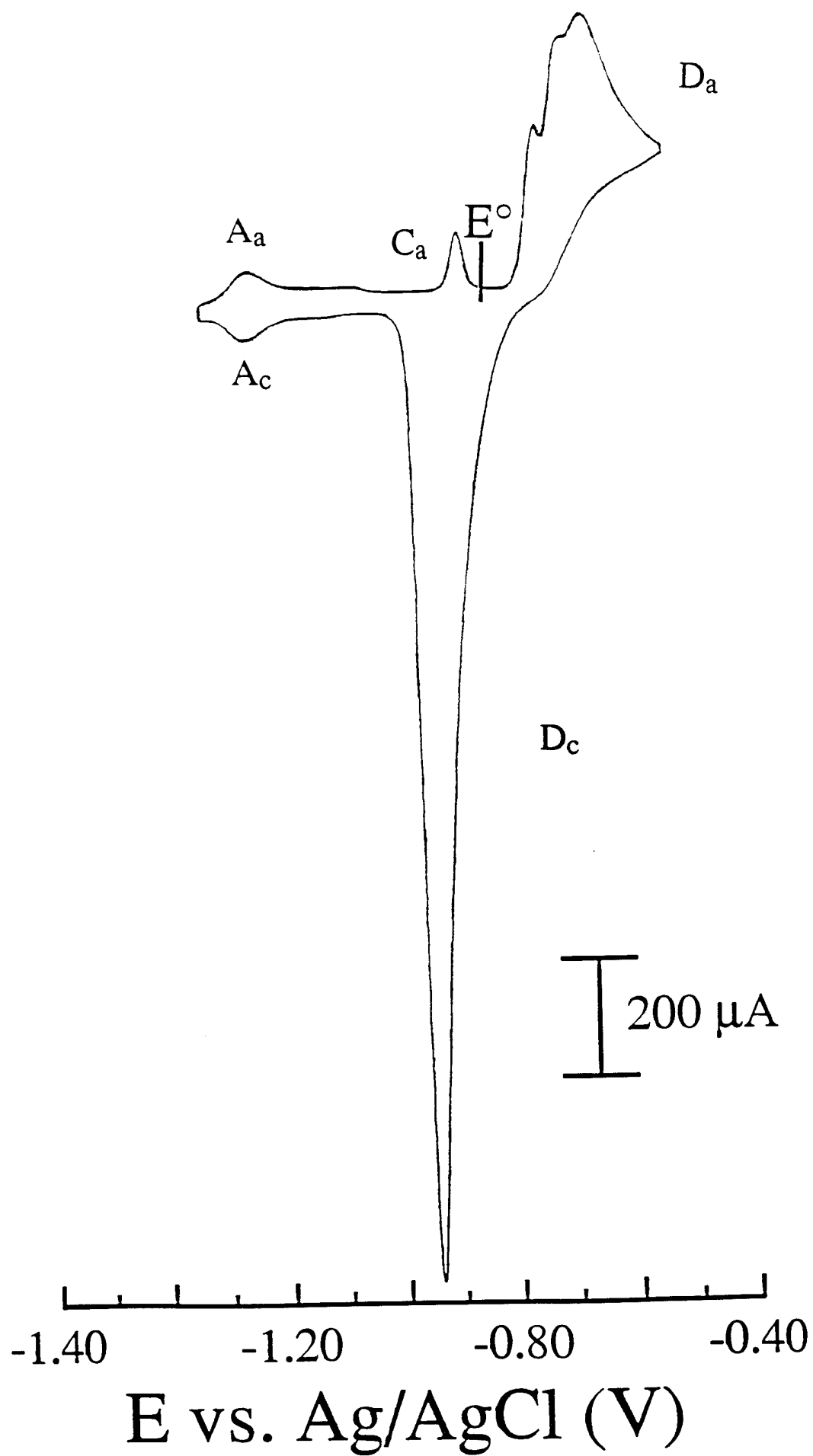
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25. The structure of Ag<sub>2</sub>S is monoclinic with angles  $\alpha = \gamma = 90^\circ \neq \beta = 125.48^\circ$ . The dimensions of the unit cell are  $a = 4.23 \text{ \AA}$ ,  $b = 6.93 \text{ \AA}$ , and  $9.53 \text{ \AA}$ , respectively. Using these values, the thickness of a Ag<sub>2</sub>S layer can be calculated as  $d = 7.8 \text{ \AA}$ . The thickness of the bulk Ag<sub>2</sub>S film is computed using this value and the density of Ag<sub>2</sub>S (7.326 g/cm<sup>3</sup>).
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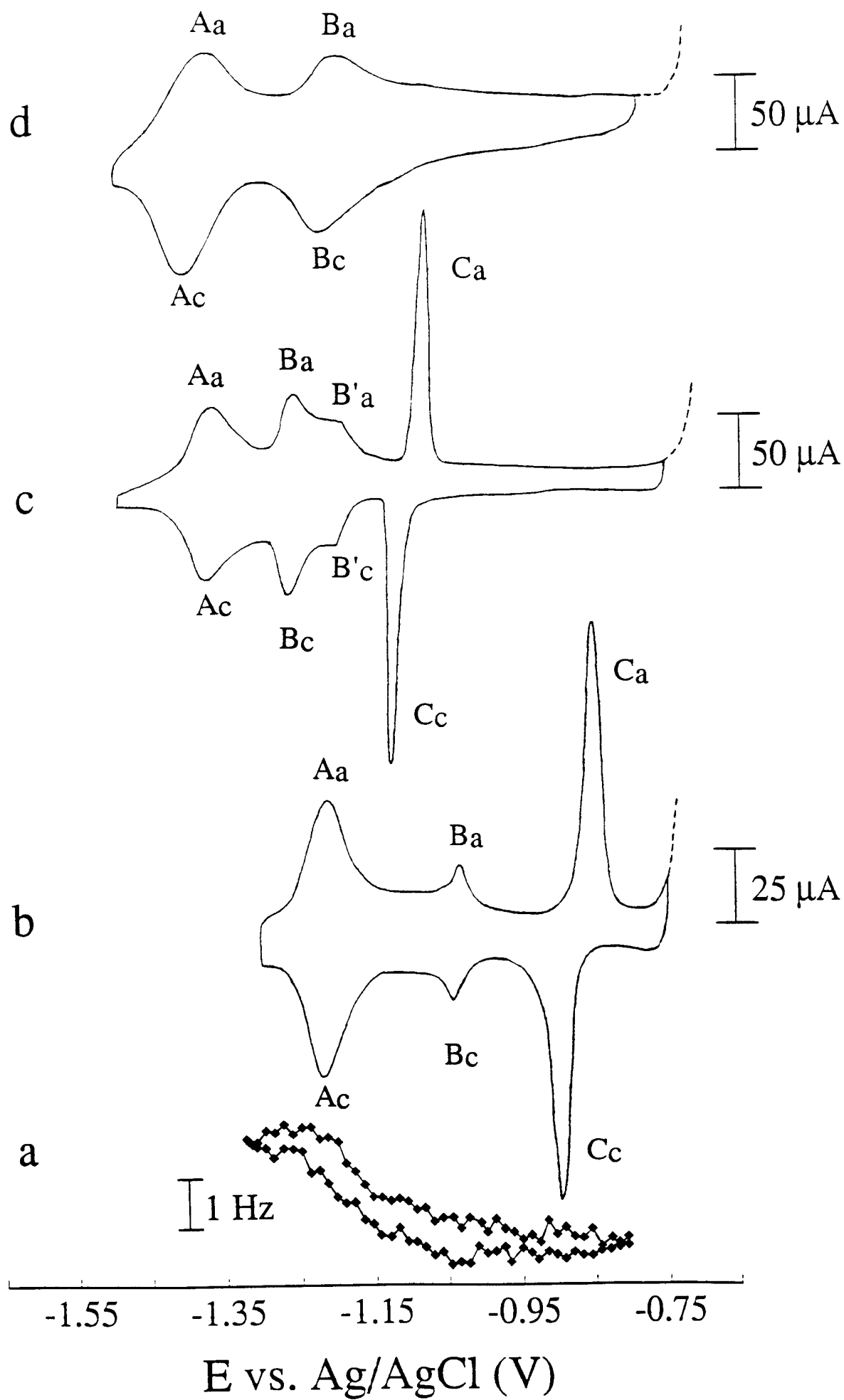


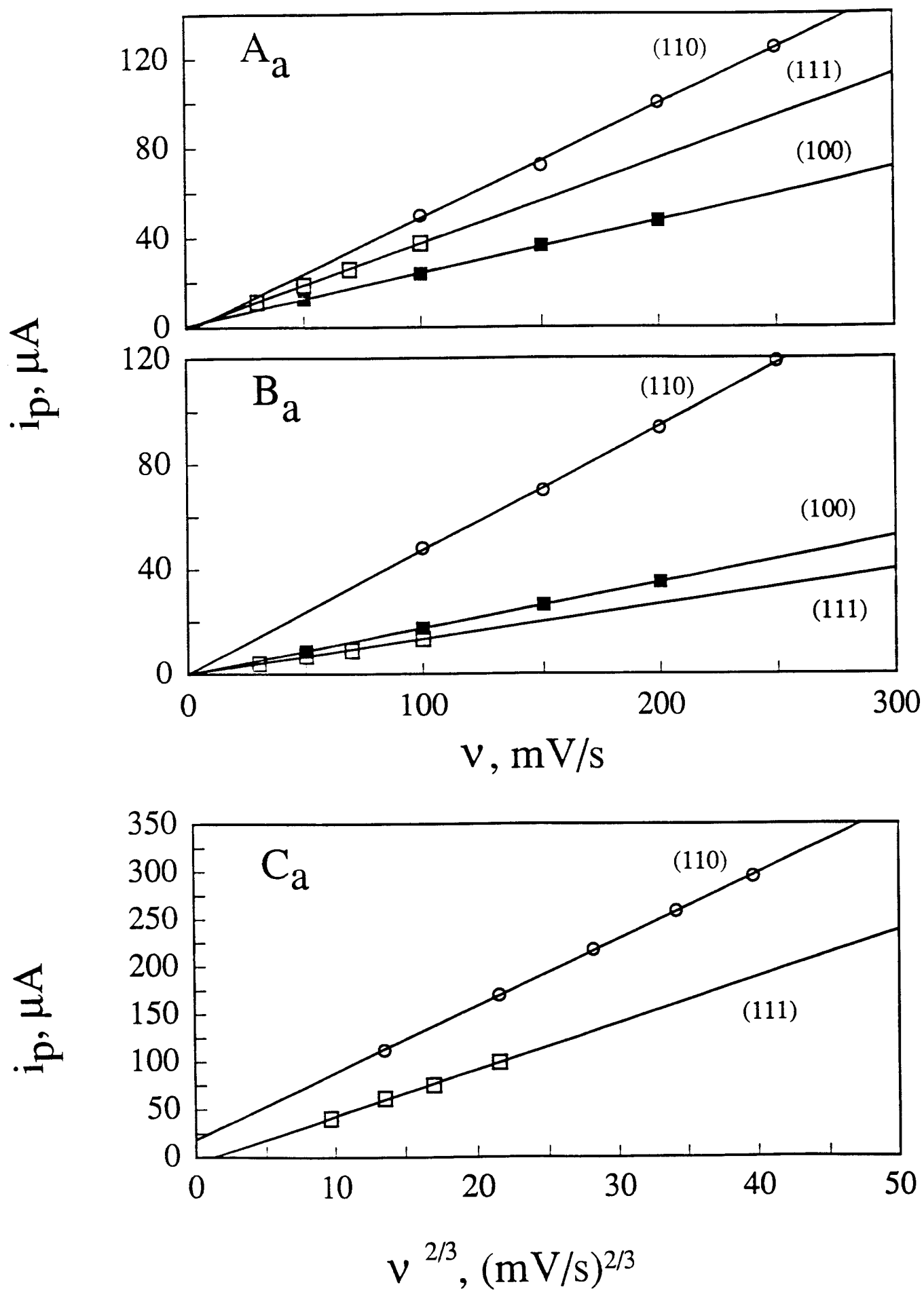
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### Figure Captions

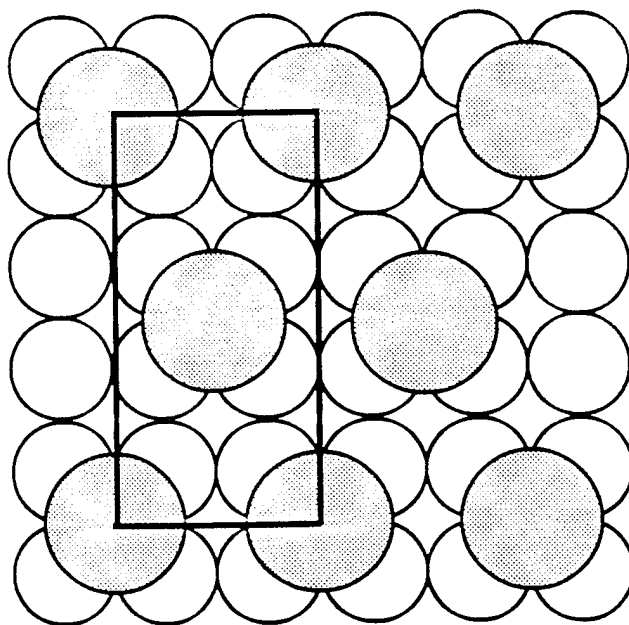
1. Voltammetric response of Ag(111) single crystal electrode ( $0.64 \text{ cm}^2$ ) in a  $\text{N}_2$ -purged solution containing  $0.75 \text{ mM Na}_2\text{S}$  and  $0.2 \text{ M NaOH}$ . Scan rate =  $100 \text{ mV/s}$ .  $\text{HS}^-$  is the primary sulfur species in the solution ( $>99.99 \%$ ).
2. (a) Potential-dependent frequency response of a Ag(111)-coated quartz crystal in a  $\text{N}_2$ -purged solution containing  $0.75 \text{ mM Na}_2\text{S}$  and  $0.2 \text{ M NaOH}$ . Voltammetric response of (b) Ag(111), (c) Ag(110), and (d) Ag(100) single-crystal electrodes in the same solution. Scan rate:  $v = 100 \text{ mV/s}$  for (b) and (c), and  $v = 200 \text{ mV/s}$  for (d).
3. Anodic peak currents as a function of potential scan rate for each of the three low-index Ag surfaces. The exposed surface areas were: (111)  $0.30 \text{ cm}^2$ ; (110)  $0.64 \text{ cm}^2$ ; and (100),  $0.64 \text{ cm}^2$ .
4. Proposed packing models of HS on the three low-index surfaces of Ag.



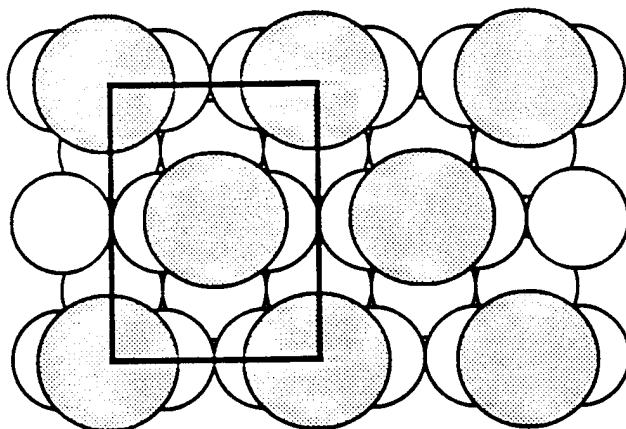




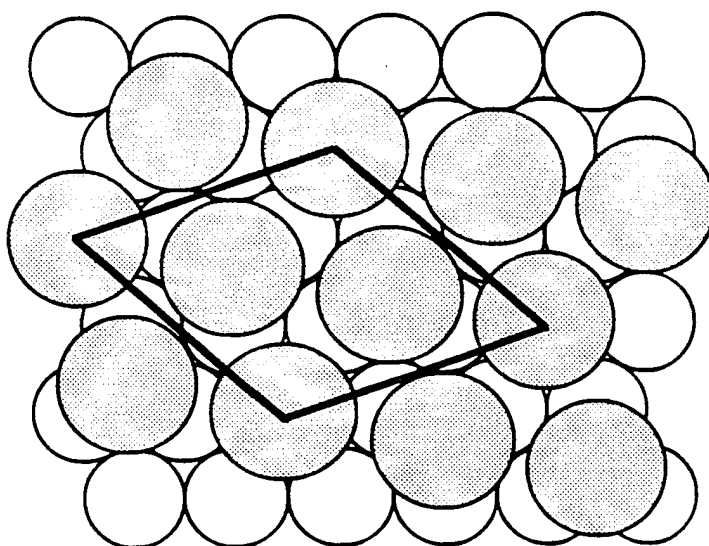
(100)  
c(2 x 4)



(110)  
c(2 x 3)



(111)  
( $\sqrt{7} \times \sqrt{7}$ )R10.9°



● = Sulfur      ○ = Silver